AD-A252 408

OFFICE OF NAVAL RESEARCH

Principal Investigator: **R. Stanley Williams**
Organization: **Regents of the University of California**

TECHNICAL REPORT No. 17

AFM STUDY OF FILM GROWTH KINETICS IN HETEROEPITAXY

by

W.M. Tong, E.J. Snyder, R.S. Williams, A. Yanase, Y. Segawa and M.S. Anderson

Prepared for publication in

Surface Science

University of California, Los Angeles

Department of Chemistry & Biochemistry and Solid State Sciences Center

Los Angeles, CA 90024-1569

DTIC
S ELECTE
JUL 0 6 1992
D

(

92 (() 4 7

92-17477

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 28 April 1992	3. REPORT TYPE AND DATES COVERED Technical 6/1/91–5/31/92

4. TITLE AND SUBTITLE
AFM STUDY OF FILM GROWTH KINETICS IN HETEROEPITAXY

5. FUNDING NUMBERS
N00014-90-J-1178

6. AUTHOR(S)

W.M. tong, E.J. Snyder, R.S. Williams, A. Yanase, Y. Segawa and M.S. Anderson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Regents of the University of California
University of California
405 Hilgard Ave.
Los Angeles, CA 90024

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report # 17

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Chemistry Program
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Prepared for publication in "Surface Science"

12a. DISTRIBUTION AVAILABILITY STATEMENT

Approved for public release.
Distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The growth of $CuCl/CaF_2$ heterostructures has been studied with an atomic force microscope (AFM). We have grown by molecular beam epitaxy (MBE) CuCl thin films at various substrate temperatures and thicknesses on $CaF_2(111)$ substrates. AFM studies reveal that islanding is the dominent growth mechanism. We calculated the height-height correlation function, $\langle |h(q,t)|^2 \rangle$, for each of our films and compared them to the predictions made by the Shadowing Growth Theory, a preexisting growth model that enabled us to extract the important kinetic parameter of surface diffusion length for the growth condition of each of the four films.

14. SUBJECT TERMS

15. NUMBER OF PAGES
8 pages

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

AFM STUDY OF FILM GROWTH KINETICS IN HETEROEPITAXY

WILLIAM M. TONG,* ERIC J. SNYDER,* R. STANLEY WILLIAMS,*
AKIHISA YANASE,† YUSABURO SEGAWA,† MARK S. ANDERSON§
*Department of Chemistry & Biochemistry/Solid State Science Center,
 UCLA, Los Angeles, California 90024-1549 USA
†Photodynamics Research Center, Frontier Research Program, RIKEN,
 ICR Building. 663 Minami-Yoshinari, Aoba-ku, Sendai, 989-32 Japan
§Space Materials Science & Technology Section,
 Jet Propulsion Laboratory, Pasadena, California 91109-8099 USA

ABSTRACT

The growth of $CuCl/CaF_2$ heterostructures has been studied with an atomic force microscope (AFM). We have grown by molecular beam epitaxy (MBE) CuCl thin films at various substrate temperatures and thicknesses on $CaF_2(111)$ substrates. AFM studies reveal that islanding is the dominant growth mechanism. We calculated the height-height correlation function, $\langle |h(q,t)|^2 \rangle$, for each of our films and compared them to the predictions made by the Shadowing Growth Theory, a preexisting growth model that enabled us to extract the important kinetic parameter of surface diffusion length for the growth condition of each of the four films.

INTRODUCTION

Both thermodynamics and kinetics play key roles in determining how film growth proceeds. The thermodynamics behind heteroepitaxial film growth are well known, at least on a theoretical level: the surface and interfacial energies of the substrate and the depositing material, all thermodynamic factors, dictate whether growth proceeds in the Franck-van der Merwe mode (layer-by-layer), the Stranski-Krastanov mode, or the Volmer-Weber mode (both islanding). Kinetics plays an equally important role in film growth: an important case is that the island formation must be limited by kinetic factors, such as surface diffusion. Yet, our theoretical understanding of the *kinetics* of film growth is still limited. A macroscopic description began in the 1950's. Konig and Helwig were the first to point out the geometrical shadowing effect [1]: protruding parts of a surface shield lower-lying regions and would in time enhance the roughness of a surface. This roughening mechanism competes with various sintering or smoothening mechanisms, the most prominent one being surface diffusion, as discussed by Herring [2]. This leads to the Shadowing Growth Theory advanced by Karunasiri, Bruinsma, and Rudnick [3-6], who accounted for the stochastic nature of deposition by including a shot noise term in a linear response theory treatment.

We are interested in CuCl because of its non-linear optical properties: CuCl excitons have a very high binding energy of 200 meV and are responsible for optical bistability of CuCl. Previous research in our group has shown that the

photoluminescence lifetimes of *quantum-confined* CuCl excitons are very short (<40 ps) [7,8], which makes CuCl thin films potential building blocks for a fast optical switching device. CaF_2 was chosen as the substrate because of its low lattice mismatch with CuCl (<1 %) and its high bandgap (ca. 10 eV). Since the optical characteristics of these quantum wells depends strongly on their thickness, our ultimate goal is to grow CuCl quantum wells that are *both* thin and uniform. However two factors conspire to prevent us from doing so. At substrate temperatures *below* 110°C, the deposited CuCl always yielded spotty Reflection High-Energy Electron Diffraction (RHEED) patterns; we suspected that they were the result of islanding, as we did not expect to have a perfect surface after growth. However, at substrate temperatures *above* 110°C, the CuCl has a very low sticking coefficient to the surface. In this work, we utilized an atomic force microscope (AFM) to obtain topographs of our CuCl thin films grown on $CaF_2(111)$ substrates and then invoked the Shadowing Growth Theory to extract kinetic as well as thermodynamic information of our system.

EXPERIMENTAL PROCEDURES

All films analyzed in this work were grown at RIKEN in an Iriekoken Molecular Beam Epitaxy (MBE) chamber equipped with a quartz crystal oscillator, RHEED, CuCl and CaF_2 Knudsen cells, and other standard ultra high vacuum (UHV) accessories. The four films used in this study were all grown on $CaF_2(111)$ substrates. After being loaded into the chamber, all four substrates were annealed in UHV at 800°C for at least 2 hours to give streaky RHEED patterns. During deposition, two of the films were held at 80°C, the other two at 110°C. At each substrate temperature, one substrate received a molecular fluence sufficient to deposit a uniform CuCl film 60 Å thick, the other substrate enough to deposit a film 120 Å thick. The flux of the CuCl beam was maintained at a fluence to deposit a 25 Å thick layer per minute approximately for all four samples. Each film yielded a spotty RHEED pattern during growth. After growth, the films were withdrawn from the chamber, quickly transferred into a desiccator, and then transported to UCLA for further analysis. The AFM investigations of the films were made in air at room temperature with a Digital Instruments Nanoscope II atomic force microscope at the Jet Propulsion Laboratory.
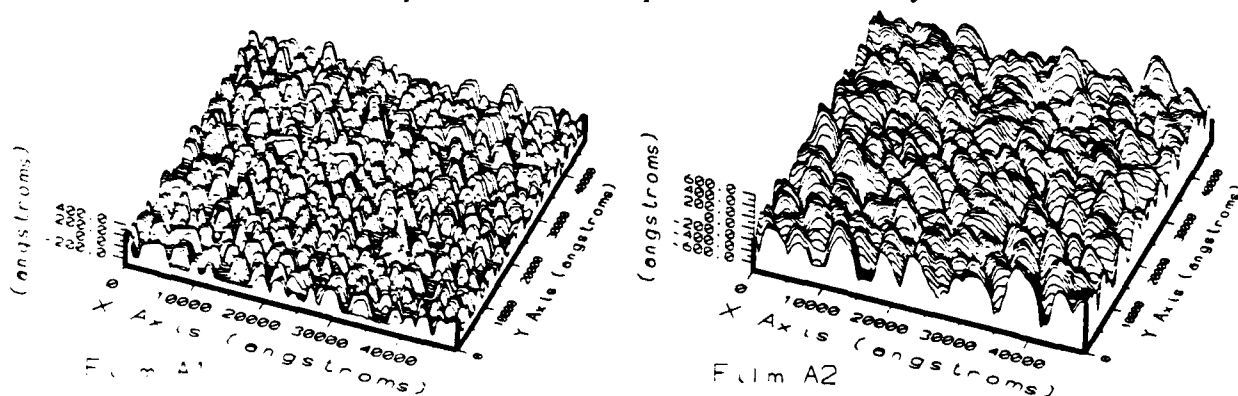

Fig. 1A: 50,000 Å by 50,000 Å AFM topographs of CuCl thin film on $CaF_2(111)$ substrate grown at (A1) 110°C, 60 Å, (A2) 110°C, 120 Å.
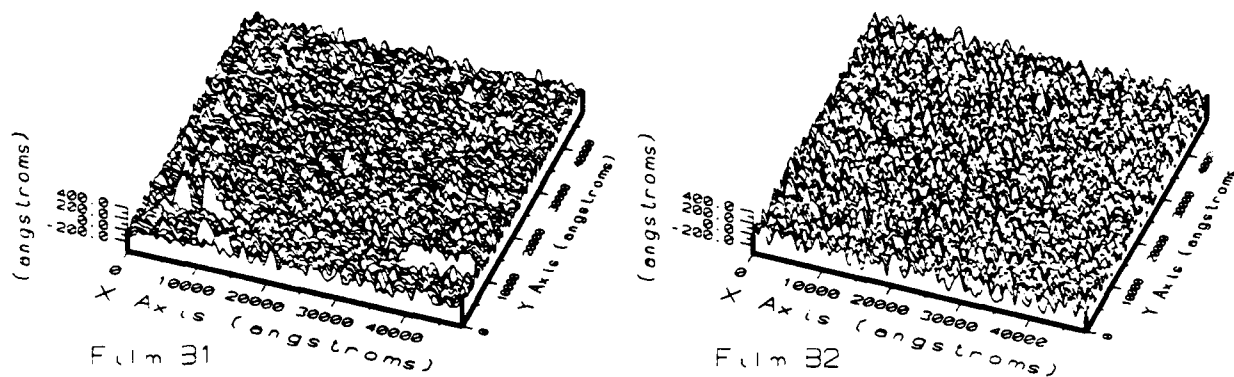
A-1

Fig.1B: 50,000 Å by 50,000 Å AFM topographs of CuCl thin film on CaF$_2$(111) substrate grown at (B1) 80°C, 60 Å, and (B2) 80°C, 120 Å.

RESULTS AND DISCUSSION

The AFM topographs of the four films are shown in in Figs.1A & 1B. The AFM topographs are 50,000 Å by 50,000 Å scans, with the z scale magnified 10 times compared to the x and y scale to enhance the surface features. It is clear from these topographs that islanding is the predominant growth mode under our deposition conditions.

To gain a further understanding of the kinetics in our data, we shall compare our results to the Shadowing Growth Theory, advanced by Karunasiri, Rudnick, and Bruinsma [3-6]. It quantifies the three-dimensional morphologies of a growing film into a two-dimensional mathematical form: the height-height correlation function, wherefrom we can extract specific kinetic and even thermodynamic information of the growth system. Our research group has already employed a modified form of this theory to study sputtered surfaces [9-12], as sputtering differs from growth only in that it involves removal rather than addition of material. The starting point of the theory is the Shadowing Growth Equation [3,6]:

$$\frac{\partial H(r,t)}{\partial t} = + J\theta(r,\{H\}) - D\nabla^4 H + \eta(r,t). \qquad (1)$$

The evolution of the real space height function H(r,t) describing the substrate surface is governed by three factors during film growth: flux, surface diffusion, and noise. In the first term, J is the flux of the depositing material and θ is the exposure angle at the point r; one key point in the Shadowing Theory is that the rate of growth of any point is proportional to how exposed (or how unshadowed) that point is to the incoming flux. The second term is the divergence of the surface diffusion current, which describes the effects of surface diffusion; D is proportional to the diffusion constant, or more precisely, $D = D_s\gamma\Omega^2 r/k_B T$, with D_s the surface diffusion constant, Ω the atomic volume, r the number of surface atoms per area, and γ the surface energy per area. The third term in the equation is a noise term that accounts for the shot noise in the arrival of the depositing species and the thermal noise of the substrate. Fourier transforming this equation converts it into a first order differential equation which can be solved analytically.

The resultant reciprocal space height-height correlation function is

$$\langle |h(q,t)|^2 \rangle \propto \frac{J\{1-e^{[-2(D|q|^4+J|q|)t]}\}}{D|q|^4+J|q|}. \tag{2}$$

One particular consequence of eq. (2) is that at large q, $\langle |h(q,t)|^2 \rangle$ will be dominated by the $D|q|^4$ term, i.e., as $q \to \infty$, the expression simplifies to $\langle |h(q,t)|^2 \rangle \to J/D|q|^{-4}$, and if we plot $\langle |h(q,t)|^2 \rangle$ vs. q on a log-log scale, we should see at large q a straight line with a slope of -4.

    The calculation of the reciprocal space correlation function from an AFM topograph has been described elsewhere [11,12]. Briefly, it is the Fourier transform of the autocovariance function,

$$G(|r_2-r_1|) = \langle H(r_2)H(r_1) \rangle - \langle H(r) \rangle^2, \tag{3}$$

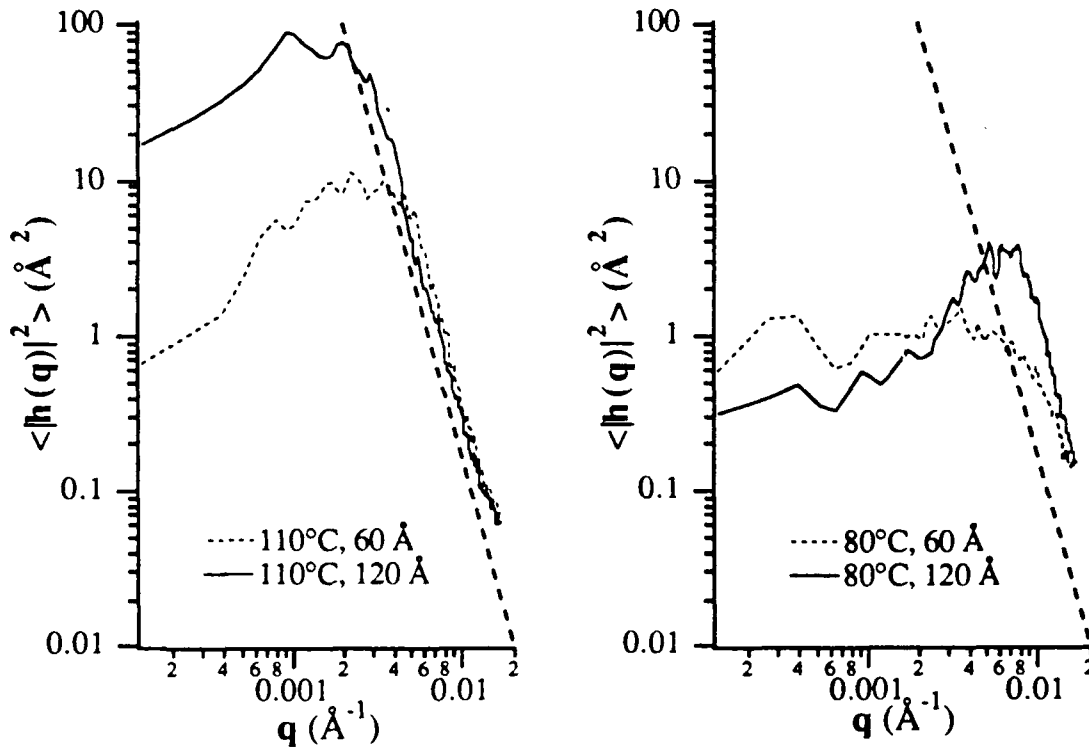where $\langle H(r) \rangle^2$ is the squared average height of the film.

Fig.2: Reciprocal space height-height correlation functions for Films
A1, A2, B1, and B2. The heavy dashed lines denote a slope of -4.
The range at which the slope is -4 represents the reciprocal length
scales where diffusion dominates the surface morphology.

The reciprocal space height-height correlation functions calculated for the four topographs are shown in Fig.2 on a log-log scale. In all four cases, the value of $\langle |h(q)|^2 \rangle$ remains constant for small q, but starts to decrease with a slope of -4 for large q. Three of the curves possess a broad peak in the region before the drop begins. The significance of these broad peaks will be discussed below. The

agreement with a -4 slope for large q is extremely good. From the Shadowing Growth Theory, the -4 slope must be a result of surface diffusion, and the q at which the -4 slope begins represents the maximum range at which surface diffusion dominates the film morphology under the growth conditions of that film. The length $r_d = 2\pi/q_d$ is the maximum distance a deposited species diffuses on the substrate. We shall call this the *diffusion length* of the deposited species. This is not to be confused with the *diffusion displacement,* which is $\sqrt{4Dt}$, and has a direct, explicit dependence on time. In our case, the diffusion length of a species is dependent not directly on time, but on the rate it loses energy to the substrate via phonon emission and on the likelihood of it meeting a preexisting well formed island during the random site hopping. To our knowledge, no other method has enabled one to measure the diffusion length of a deposited species on a substrate. This is a remarkably simple, if not unique way to deduced this kinetic parameter. The diffusion lengths calculated for the high fluence films (A2,B2) approximate those for CuCl on CuCl, while the diffusion lengths calculated for the low fluence films (A1,B2) approximate those for CuCl on CaF$_2$(111). They are listed in Table I below.

Table I. Numerical experimental data collected for the CuCl films on CaF$_2$(111) substrates.

Substrate Temp.	110°C		80°C	
Film	A1	A2	B1	B2
Nominal Fluence	60 Å	120 Å	60 Å	120
Diffusion Length (q_d) (r_d)	5.5×10^{-3}Å^{-1} (1,100 Å)	4.5×10^{-3}Å^{-1} (1,400 Å)	1.2×10^{-2}Å^{-1} (520 Å)	1.1×10^{-2}Å^{-1} (570 Å)
Position of Peak	2.5×10^{-3}Å^{-1} (2,500 Å)	1×10^{-3}Å^{-1} (6,300 Å)	--	6×10^{-3}Å^{-1} (1,050 Å)

In three of the four height-height correlation plots, broad peaks occur just before the curve begins to follow the -4 slope. Their existence is not predicted by the Shadowing Growth Theory. These broad peaks represent enhanced correlation and appear at length scales that are just longer than the surface diffusion length. We believe they are the consequences of islanding, a thermodynamic phenomenon which the Shadowing Growth Theory does not take into account. The reason islanding introduces enhanced correlation at these length scales is because the islands have characteristic sizes, as dictated by the thermodynamic parameter of surface energy, and characteristic separations, as dictated by the kinetic parameter of diffusion length. The position and width of the broad peak represents the length scales and the spread in length scales at which these correlations occur.

CONCLUSIONS

In this study, we have demonstrated that that it is possible to extract quantitative information from topographic data. Our work, though preliminary and rough, has yielded important kinetic information related to film growth and morphology. We are hopeful that systematic studies of this type will eventually

lead us to a fuller understanding of thin film growth.

REFERENCES

1. H. Konig and G. Helwig, Optik, 14, 83 (1954).

2. C. Herring, J. Appl. Phys., 21, 301 (1950).

3. R.P.U. Karunasiri, R. Bruinsma, J. Rudnick, Phys. Rev. Lett., 62, 788 (1989).

4. *ibid*, in Non-linear Structures in Physical Systems, edited by L. Lam and H. C. Morris (Springer, New York, 1990).

5. G. S. Bales, R. Bruinsma, J. Rudnick, R. S. Williams, Science, 249, 264, (1990).

6. R. P. U. Karunasiri, Ph.D. Thesis, UCLA Physics (1991).

7. R. S. Williams, D. K. Shuh, Y. Segawa, J. Vac. Sci. Tech. A., 6, 1950 (1988).

8. D. K. Shuh, R. S. Williams, Yusaburo Segawa, Jun-ichi Kusano, Yoshinobu Aoyagi, Susumu Namba, Phys. Rev. B., 44, 5827 (1991).

9. E. A. Eklund, R. Bruinsma, J. Rudnick, R. S. Williams, Phys. Rev. Lett., 67, 1759 (1991)

10. E. A. Eklund, R. S. Williams, E. J. Snyder, Mat. Res. Soc. Symp. Proc., 157, 305 (1990).

11. E. A. Eklund, E. J. Snyder, R. S. Williams, Surf. Sci., (in press).

13. E. A. Eklund, Ph.D. Thesis, UCLA Physics (1991).